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Static form function of an entangled polymer in a strained state (melt or rubber)

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Abstract. — The article contains a complete analytical solution of the static form function of an entangled polymer in a strained state. The entanglements, or stress points, undergo an affine deformation and remain afterwards fixed. The other parts of the chain are relaxed and Brownian. The parameters are \( \langle S \rangle \) and \( N \), where \( \langle S \rangle \) is the mean value of the Brownian area \( S \) between entanglements and \( N \) is the number of entanglements per chain. The results agree with experiments on polystyrene and are consistent with other data concerning this polymer.

1. Introduction.

It is well known that the measurement of the dynamic or static form factor of entangled polymers deals with times of the order of nanoseconds, whereas the reptation times are of the order of seconds. Thus, the entanglements can be considered as fixed with respect to the polymer, for times of the order of nanoseconds.

Of course, the same approximation applies to rubbers and, in this case, the simple approximation corresponds to the junction affine model. In fact, the short time identity of behaviour for melts and for rubbers was verified by Boué et al. [1] who found experimentally that the form factor of a rubber and of its parent melt coincide.

Very recently, the author calculated the dynamic function of a labelled polymer in an entangled melt [2] and he found good agreement with the experiment. He now wants to apply the same approximation here, in order to calculate the static form function \( S(q) \) of a labelled polymer in an entangled and strained melt. The aim is to see how good the approximation is in this case. Actually, the problem has been considered already in 1982 by Ullman [3] et reconsidered in 1988 by Higgs and Ball [4]. However, these authors do not make the entire calculation precisely and they compute results numerically. Nevertheless, it is possible to obtain exact formulae corresponding to the approximation and this is done here.

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2. The model.

We consider that each polymer contains $N$ entanglements. The value of $N$ (which need not be an integer) is fixed for all polymers in the melt. This is an approximation but it can be considered as the only one in the article.

The mean square distance between entanglements which are nearest neighbours on a polymer is a random variable

$$\langle (r_{j+1} - r_j)^2 \rangle = 3 S_{j+1}$$

(1)

$S_j$ is proportional to the "number of links" between entanglements. The entanglements are supposed to be distributed at random on the polymer. Thus all the $S_j$ are independent variables and the probability law $P(S_j)$ is

$$P(S) = \frac{1}{\langle S \rangle} \exp(-S/\langle S \rangle)$$

(2)

The total "length" of the chain is proportional to $S_T$

$$S_T = \sum_{j=1}^{N+1} S_j$$

($r_0$ and $r_{N+1}$ correspond to the extremities; see Fig. 1). Thus

$$\langle S_T \rangle = (N + 1)\langle S \rangle$$

$$\langle [S_T - \langle S_T \rangle]^2 \rangle = (N + 1)\langle S \rangle^2$$

![Diagram](image)

**Fig. 1.** — A chain for $N = 3$ with the coordinates $r_1$, $r_2$, $r_3$ of the entanglement points and the Brownian areas $S_1$, $S_2$, $S_3$, $S_4$.

Therefore the polydispersity of the chains is

$$p = \frac{M_w}{M_n} = \frac{\langle S_T^2 \rangle}{(S_T)^2} = 1 + \frac{1}{N + 1}$$

and goes to one when $N$ goes to infinity.
The melt is strained at time zero
\[
\begin{align*}
    x &\longrightarrow x/\sqrt{\lambda} \\
    y &\longrightarrow y\lambda \\
    z &\longrightarrow z/\sqrt{\lambda}
\end{align*}
\]

Then, after waiting for a time \(t_0\) with \(\tau > t_0 > \tau_R\), where \(\tau\) is the reptation time and \(\tau_R\) the Rouse time, the form function of a labelled chain is measured
\[
S(q) = \frac{1}{S_T} \int_0^{S_T} ds \int_0^{S_T} ds' \exp \left\{ i q \cdot [r(s) - r(s')] \right\}
\]
This is the quantity which we want to evaluate.

Therefore, we may put \(q_z = 0\) and, for a strain \(\lambda\) and a polymer with \(N\) entanglements, we define
\[
S(q_x, q_y; \lambda, N) \equiv S(q)
\]

Since we deal with Gaussian variables, we want precisely to calculate
\[
S(q_x, q_y; \lambda, N) = \frac{1}{\langle S_T \rangle_P} \left\langle \int_0^{S_T} ds \int_0^{S_T} ds' \exp \left\{ -\frac{q_x^2}{2} \left\langle [x(s) - x(s')]^2 \right\rangle_G - \frac{q_y^2}{2} \left\langle [y(s) - y(s')]^2 \right\rangle_G \right\} \right\}
\]  \hspace{1cm} (3)
where \(\langle \rangle_G\) represents an average over Gaussian variables and \(\langle \rangle_P\) an average over polydispersity (i.e. by using \(P(S)\) given by (2)).

Then setting
\[
\begin{align*}
    q_x &= q \sin \theta \\
    q_y &= q \cos \theta
\end{align*}
\]
and defining
\[
f(\theta) = \lambda^2 \cos^2 \theta + \lambda^{-1} \sin^2 \theta - 1
\]
we shall express \(S(q_x, q_y; \lambda, N)\) in terms of \(\lambda, N, f(\theta)\) and \(Z\) where
\[
Z = \frac{q^2 \langle S \rangle}{2}
\]  \hspace{1cm} (4)

Formula (3) gives the form function after a time \(t_0\) with \(\tau > t_0 > \tau_R\) since we average over the Gaussian variables (keeping the stress points fixed).

3. Calculation of \(S(q_x, q_y; \lambda, N)\).

The points of abscissas \(s\) and \(s'\) may belong to the same subchain between entanglements or to different subchains. Therefore, we define two integrals \(I_0(f)\) and \(I_1(f)\) corresponding to these two cases
\[
I_0(f) = \langle I_0(S, f) \rangle_P = \int_0^{\infty} dS \ P(S) \ I_0(S, f)
\]
\[
I_1(f) = \langle I_1(S, f) \rangle_P = \int_0^{\infty} dS \ P(S) \ I_1(S, f)
\]
\[
I_0(S, f) = \frac{1}{\langle S \rangle^2} \int_0^{S} ds \int_0^{S} ds' \exp \left\{ -\frac{q_x^2}{2} \left\langle [x(s) - x(s')]^2 \right\rangle_G - \frac{q_y^2}{2} \left\langle [y(s) - y(s')]^2 \right\rangle_G \right\}
\]
\[
I_1(S, f) = \frac{1}{\langle S \rangle} \int_0^{S} ds \exp \left\{ -\frac{q_x^2}{2} \left\langle x^2(s) \right\rangle_G - \frac{q_y^2}{2} \left\langle y^2(s) \right\rangle_G \right\}
\]  \hspace{1cm} (5)
(in the second integral, we assume that \( x(0) = y(0) = 0 \).

We sum all the contributions (the contributions containing \( I_1(0) \) come from dangling bonds).

We find

\[
\frac{N + 1}{(S)} S (q_x, q_y; \lambda, N) = (N - 1) I_0(f) + 2 I_0(0) + \frac{2A}{A - 1} \left[ N - 2 - \left( \frac{1 - A^{-N+2}}{A - 1} \right) \right] [I_1(f)]^2 + \frac{4A}{A - 1} \left[ 1 - A^{-N+1} \right] I_1(f) I_1(0) + 2A^{-N+1} [I_1(0)]^2
\]

where

\[
\frac{1}{A} = \left( \frac{1}{A(S)} \right)_p = \int_0^\infty dS \frac{P(S)}{A(S)}
\]

with

\[
\frac{1}{A(S)} = \exp \left[ -\frac{q^2 \sin^2 \theta \langle x^2 \rangle}{2\lambda} - \frac{q^2 \cos^2 \theta \lambda^2 \langle y^2 \rangle}{2} \right]
\]

\[
\frac{1}{A(S)} = \exp \left[ -\frac{q^2 S(1 + f(\theta))}{2} \right]
\]

Thus, applying equation (4), and taking equation (2) into account, we find

\[
A = 1 + Z + Z f(\theta)
\]

4. Calculation of \( I_0(f) \).

In order to calculate \( I_0(S, f) \), we set

\[
x(s) = \bar{x}(s) + \frac{s}{S} X \lambda^{-1/2}
\]

\[
y(s) = \bar{y}(s) + \frac{s}{S} Y \lambda
\]

where \( \bar{x}(s) \) and \( \bar{y}(s) \) represent the fluctuating undeformed parts of \( x(s) \) and \( y(s) \) with

\[
\bar{x}(0) = \bar{x}(s) = 0
\]

\[
\bar{y}(0) = \bar{y}(s) = 0
\]

Then

\[
q_x^2 \left( [x(s') - x(s)]^2 \right) + q_y^2 \left( [y(s') - y(s)]^2 \right) =
\]

\[
\left( \frac{s' - s}{S} \right)^2 \left[ q_x^2 \lambda^{-1} \langle X^2 \rangle_G + q_x^2 \lambda^2 \langle Y^2 \rangle_G \right] + q_x^2 \left( [\bar{x}(s') - \bar{x}(s)]^2 \right)_G + q_y^2 \left( [\bar{y}(s') - \bar{y}(s)]^2 \right)_G =
\]

\[= q^2 \left[ \frac{(s' - s)^2}{S} [1 + f(\theta)] + \frac{|s' - s| (S - |s' - s|)}{S} \right] \]

Therefore

\[
I_0(S, f) = \frac{1}{(S)^2} \int_0^S ds' \int_0^S ds \exp \left\{ -\frac{q^2}{2} \left[ \frac{(s' - s)^2}{S} (1 + f(\theta)) + \frac{|s' - s| (S - |s' - s|)}{S} \right] \right\}
\]

\[= \frac{2S^2}{(S)^2} \int_0^1 d\sigma (1 - \sigma) \exp \left\{ -\frac{q^2 S}{2} \left[ \sigma + \sigma^2 f(\theta) \right] \right\}
\]
Then, according to equations (5) and (2), we obtain

\[ I_0(f) = 4 \int_0^1 \frac{1 - \sigma}{[1 + Z\sigma + Zf(\theta)\sigma^2]^3} \, d\sigma \]  

(8)

The integral can be calculated by expanding the integrand with respect to \( \frac{1}{\sigma - \sigma'} \) and \( \frac{1}{\sigma - \sigma''} \). In the result, fictitious poles appear for \( \sigma' - \sigma'' = 0 \) and they have to be reduced. Thus, in order to express the results in a simple form, it is convenient to set

\[ T(x) = \frac{1}{\sqrt{x}} \text{Arg th} \left( \sqrt{x} \right) \quad (x > 0) \]
\[ = \frac{1}{\sqrt{-x}} \text{Arg tg} \left( \sqrt{-x} \right) \quad (x < 0) \]

(9)

\( T(x) \) is an analytical function of \( x \), for all real \( x \). In fact, we see that near \( x = 0 \), it has an expansion

\[ T(x) = 1 + \frac{x}{3} + \frac{x^2}{5} + \ldots \]

The results will be expressed in term of \( B(x) \)

\[ B(x) = \frac{3}{x} [T(x) - 1] \]  

(10)

with \( B(0) = 1 \).

Then, after rather lengthy algebra, we find

\[ I_0(f) = \frac{2}{(2 + Z)^3} \left[ \frac{(2 + Z)^3 + Z (4 + 3Z + Z^2) f(\theta) - 2Z^2 f(\theta)}{1 + Z + Zf(\theta)} \right] \]

\[ + \frac{8Z}{(2 + Z)^3} \frac{f(\theta)[1 + 2f(\theta)]}{Z - 4f(\theta)} \left[ B \left( \frac{Z}{(2 + Z)^2} [Z - 4f(\theta)] \right) - 1 \right] \]  

(11)

and for \( f(\theta) = 1 \)

\[ I_0(0) = \frac{2}{1 + Z} \]  

(12)

5. Calculation of \( I_1(f) \).

In order to calculate \( I_1(S, f) \), we proceed as in the preceding section

\[ x(s) = \tilde{x}(s) + \frac{S}{S} X \lambda^{-1/2} \]
\[ y(x) = \tilde{y}(s) + \frac{S}{S} Y \lambda \]
Then
\[ q_x^2 \langle x^2(s) \rangle + q_y^2 \langle y^2(s) \rangle = \frac{s^2}{S^2} \left[ q_x^2 \lambda^{-1} \langle X^2 \rangle_G + q_y^2 \lambda^2 \langle Y^2 \rangle_G + q_x^2 \langle x^2(s) \rangle_G + q_y^2 \langle y^2(s) \rangle_G \right] \]
\[ = q^2 \left[ \frac{s^2}{S}(1 + f(\theta)) + \frac{s(S-s)}{S} \right] \]

Therefore
\[ I_1(S, f) = \frac{1}{\langle S \rangle} \int_0^\infty ds \exp \left\{ -\frac{q^2}{2} \left[ \frac{s^2}{S}(1 + f(\theta)) + \frac{s(S-s)}{S} \right] \right\} \]
\[ = \frac{S}{\langle S \rangle} \int_0^1 d\sigma \exp \left\{ -\frac{q^2 S}{2} [\sigma + \sigma^2 f(\theta)] \right\} \]

According to equations (5) and (2), we obtain

\[ I_1(f) = \int_0^\infty \frac{d\sigma}{[1 + Z \sigma + Zf(\theta)\sigma^2]^2} \]

This integral is calculated in the same way as \( I_0(f) \) and the result is expressed in terms of \( B(x) \) given by equations (10) and (9). We find

\[ I_1(f) = \frac{2 + Z + Zf(\theta)}{(2 + Z)[1 + Z + Zf(\theta)]} - \frac{4Zf(\theta)}{3(2 + Z)^2} B \left( \frac{Z}{(2 + Z)^2} [Z - 4f(\theta)] \right) \quad (13) \]

and for \( f(\theta) = 1 \)

\[ I_1(0) = \frac{1}{1 + Z} \quad (14) \]

6. Results.

We can now put the values of \( A \) (Eq.(7)), of \( I_0(1) \) (Eq.(12)) and of \( I_1(1) \) (Eq.(14)) in equation (6), and we obtain

\[ \frac{N + 1}{\langle S \rangle} S(q_x, q_y; \lambda, N) = (N-1)I_0(f) + \frac{4}{1 + Z} \]
\[ + 2 \left[ \frac{1 + Z + Zf(\theta)}{Z[1 + f(\theta)]} \right] \left\{ N - 2 - \frac{1 - (1 + Z + Zf(\theta))^{-N+2}}{Z[1 + f(\theta)]} \right\} [I_1(f)]^2 \]
\[ + 4 \left[ \frac{1 + Z + Zf(\theta)}{Z(1 + Z)[1 + f(\theta)]} \right] \{ 1 - [1 + Z + Zf(\theta)]^{-N+1} \} I_1(f) \]
\[ + \frac{2}{(1 + Z)^2} [1 + Z + Zf(\theta)]^{-N+1} \] \quad (15)

where \( I_0(f) \) and \( I_1(f) \) are given by equations (11) and (13).

Since \( I_0(f) \) and \( I_1(f) \) are independent of \( N \), the value of the limit \( N \to \infty \) is immediate. The values of \( q^2 S(q)/2 = Z S(q)/\langle S \rangle \) are plotted in this limit in figures 2a, b, c for \( \lambda = 2, 3, 4 \) and for various values of \( \theta \). For \( N = 5 \), the values of \( q^2 S(q)/2 = Z S(q)/\langle S \rangle \) are plotted in figures 3a, b, c for the same values of \( \lambda \) and \( \theta \). We note that when we have \( f(\theta) = 0 \), i.e. when
Fig. 2. — Form functions for $\lambda = 2, 3, 4$ and $N$ infinite; the dashed line corresponds to the isotropic angle.
Fig. 3. — Form functions for $\lambda = 2, 3, 4$ and $N = 5$; the dashed line corresponds to the isotropic angle.
\[ \lambda^2 \cos^2 \theta + \lambda^{-1} \sin^2 \theta = 1 \] (\( \tan \theta = \lambda^{1/2}(1 + \lambda)^{1/2} \)) then the preceding formula gives the value for the "isotropic melt".

Using formula (15), we plot iso-intensity contours, corresponding to \( N \to \infty \) in figures 4a, b, c, and corresponding to \( N = 5 \) in figures 5a, b, c. The values of \( H = S(q) / \langle S \rangle \) are indicated on each contour. Thus, in figures 5b and 5c, we obtain the shape of "lemons" or "lozenges" that have been experimentally predicted by Boué et al. [5].

Fig. 4. — Contours \( S(q) = H \) for \( \lambda = 2, 3, 4 \) and \( N \) infinite; the value of \( H \) is plotted near the curves.
Fig. 5. — Contours $S(q) = H$ for $\lambda = 2, 3, 4$ and $N = 5$; the value of $H$ is plotted near the curves.

7. Comparison with experiments.

We compare our results with data from Lartigue, Buzier, Bastide and Boué [6]. The data are obtained with a mixture of deuterated and non-deuterated polystyrene (PSD and PSH) of volume fractions $\varphi_D = 0.0932$ and $\varphi_H = 1 - \varphi_D$. We have $M_{n,D} = 985 000$ (with $p_D = M_{W,D}/M_{n,D} = 1.09$) for PSD and $M_{n,H} = 1040 000$ (with $p_H = M_{W,H}/M_{n,H} = 1.07$) for PSH. The static form function of individual polymers is then given by the static form function of
Fig. 6. — Comparison of theory and experiment for $\lambda = 3$; it is made for the angle $\theta = 0$, $\theta = 90$ and for the isotropic angle. As parameters of the theory, we take $\langle S \rangle = 23$ and $N = 70$. The experiments are represented by diamonds, squares and crosses; normalisation is obtained by imposing that 2 is the asymptote of the isotropic data (crosses).

the melt. The polydispersity is low but still relevant.

In figure 6, we use values of $\langle S \rangle$ and $N$ which are calculated from other sources as we shall see: we take $\langle S \rangle = 23$ nm$^2$ and $N = 70$. From a fit with polystyrene data for the loss modulus $G''(\omega)$ in polystyrene samples [7], we found that the average mass between entanglements is

$$M_0 = 14,000 \text{ dalton}$$

and therefore

$$N = M/M_0 \approx 70$$

On the other hand, from the study of polystyrene solutions [8], we found

$$S = 16.6 \times 10^{-4} \times M \text{ nm}^2$$

Therefore, for the distance between entanglements, we get

$$\langle S \rangle = 16.6 \times 10^{-4} \times M_0 \text{ nm}^2 = 23.2 \text{ nm}^2$$

(Note that we find $S = 1640 \text{ nm}^2$ independently of the value of $M_0$). In this way, we obtain a reasonable fit.
8. Conclusion.

We assumed that the strain produces an affine deformation of the entanglement points which otherwise remain fixed during the observation. The results confirm the validity of this model. Note that we were not able to improve the fit by assuming any motion of the chain through entanglements. Nevertheless, the entanglements may slip and this effect could have some importance, in spite of the fact that, during relatively short times, an identical behaviour has been observed for melts and for rubbers [1]. However, we note that, by comparing the theory with experiments on low polydispersity samples, we could reach a rather good fit, impossible to obtain with previous experiments corresponding to very polydisperse systems. So before correcting our assumptions, one should first verify that the remaining discrepancy between theory and experiment is real. Moreover, similar assumptions have been very successful in another connection, namely for the derivation of the dynamical form function of polystyrene [2]. In brief, we obtain a good agreement considering the polydispersity of the sample, but the questions concerning possible entanglement slippage remain open.

References

[6] Lartigue C., Buzier M., Bastide J. and Boué F., unpublished (the author thanks F. Boué for communicating the data to him).